FACTORS AFFECTING BOILING IN A LIQUID

BY
REINHOLD FRIDTJOF LARSON
B.S., University of Illinois, 1923
M.S., University of Illinois, 1931

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SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
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FACTORS AFFECTING BOILING IN A LIQUID

INTRODUCTION

The phenomenon of ebullition, or the formation of vapor bubbles within a liquid, or on a liquid-vapor boundary has received little attention. In investigations on the transfer of heat to a boiling liquid, differences have been observed in the way that vapor bubbles form on a heated surface, and attempts have been made to correlate heat transfer coefficients with the type of boiling observed. Nucleate boiling has been associated with the wetted surface and film boiling with the unwetted surface. A slight degree of superheat of the liquid has been observed in connection with nucleate boiling, with none for film boiling. Under certain conditions, however, liquids have failed to boil at the expected temperatures, their normal boiling points, and considerable superheat of the liquid has been observed. No satisfactory theory for the occurrence of this metastable state has been advanced.

THEORY OF EBULLITION

Based on thermodynamic reasoning the author proceeds to show that the initiation of a bubble in a heated liquid is not possible without some degree of superheat. This appears to be necessary for the establishment of a liquid-vapor interface with its free interfacial energy, commonly called the surface tension. If the bubble is to form in the liquid alone the increase in free energy will be $2\sigma_{LV}$ A where σ is the free surface energy per unit area and A is the area of interface formed. This case would require the greatest superheat of the liquid. If the bubble forms on a liquid-solid boundary the increase in free energy would be $[\sigma_{LV} + (\sigma_{SV} - \sigma_{LS}]A$, where the term in parenthesis is called the adhesion free energy. This term may be either positive, zero,

or negative and determines the degree of superheat necessary for ebullition to take place. If zero or negative no superheat is required. Accurate measurement of the adhesion free energy is extremely difficult because of the heterogeneous nature of solid surfaces. However, the literature on flotation gives relative values for various substances.

EXPERIMENTAL WORK

In order to test various substances for their ability to support superheat of the liquid, the author built a test apparatus of glass, in which various solids in the form of 1/8″ balls were subjected to superheated distilled water at atmospheric pressure. This was accomplished by heating the water in an inverted glass tube from above by radiant heaters. Substances, called ebullators, whose adhesion free energy was less than that of glass could thus be tested. Temperatures were measured by means of a thermocouple in a glass capillary well, adjacent to the ebullator.

The following test results were obtained and represent the maximum temperatures reached by the water before ebullition, which was sometimes violently explosive, occurred. Very careful cleaning of the apparatus and ebullator, and preboiling, was required before superheat and consistent results could be obtained. A large number of tests were made with various methods of heating and cleaning of the ebullator. Cleaning of the ebullator was by washing in warm tri-sodium phosphate solution, and where corrosive action did not occur, by concentrated sulfuric and sodium dichromate solution, with subsequent rinsing in distilled water.

EBULLITION TEMPERATURES (AVERAGE)—°F

Monel Ball—direct radiant heat	220
Monel Ball—slower heating rate	224
Monel Ball—cleaned in chromic acid solution	236
H. C. Steel Ball—slow heating rate	221
H. C. Steel Ball—black oxidized surface	210
Copper Ball—phosphate washed	214
Brass Ball—phosphate washed	234

Brass Ball—dull surface	227
Bronze Ball—acid washed	211
Bronze Ball—surface roughened	211
Cast Iron Ball—phosphate washed	218
Aluminum Ball—bright surface Progressive increase observed	175 to 199
Aluminum Ball—dull surface Progressive increase observed	221 to 226
Aluminum Ball—surface coating removed	163
Zinc Ball—phosphate washed	188
Lead Ball—phosphate washed	206.5
Carbon Ball—made from electrode	206
Magnesium Ball—phosphate washed	112
Tin Ball—phosphate washed	214 to 219.8
Nickel Ball—acid washed	225.8
Mild Steel Ball—phosphate washed	215 to 220
Mild Steel Ball—NaOH added to water,pH= 10	220 to 235
Mild Steel Ball—$CaCo_3$ added to water, pH=8.5	230 to 239.

The last three series showed progressive increase in temperature with succeeding tests.

The surface tension of the water was changed from 72.5 dynes/cm to 54 bynes/cm by means of a wetting agent and the following results obtained:

Monel Ball	226.5
Copper Ball	223.5
Bright Carbon Steel Ball	172
Oxidized Carbon Steel Ball	223
Bright Aluminum Ball	220.5
Bright Brass Ball	228

The results obtained with an acid washed stainless steel ball were somewhat scattered, ranging from 228°F to 258°F with an average value for a great number of tests lying around 250°F. A stainless steel ball with a surface roughened with emery cloth gave an average of 253°F.

A number of tests were conducted without an ebullator other than the glass itself, and indicated a scattering of test results varying from 247°F to 288.5°F with an average of 263°F.

DISCUSSION

The results of the tests above indicate that the degree of superheat to which a pure liquid can be heated depends upon the presence of an ebullator, and that various solids differ

somewhat in their property of initiating bubble formation. The property responsible for the superheating of the liquid appears to be the interfacial free energy or surface tension for the liquid alone, and if an ebullator or solid surface is present this appears to be the adhesion free energy of the liquid-solid interface with respect to the vapor. Solid surfaces appear to be very heterogeneous in this property, and in some cases subject to change. Substances readily wetted and chemically inert or resistant to corrosion appear to support considerable superheat.

Ebullition or the formation of bubbles on a solid surface at temperatures less than the normal boiling point is probably due to liberation of hydrogen, since substances observed to do this are considerably above hydrogen in the electromotive series.

There is considerable evidence in the literature that surface energy phenomena, surface tension, adhesion tension, etc., are due to intermolecular or interatomic forces, and are of a chemical nature. If such is the case, the ebullator may be looked upon as a catylist in promoting the initiation of bubbles in a superheated liquid. There are probably no completely wetted solids due to the heterogeneous nature of their surfaces, and thus all serve as ebullators to varying degrees. The ebullition property varies inversely as the ahdesion free energy of the surface. Physical roughness of the surface in itself does not appear to be a factor in initiating bubble formation.

VITA

The author was born April 1, 1899, at Geneva, Illinois. There he received his grade and high school education, completing the latter at Geneva Public School in 1917. After two years working as a machinist he registered at the University of Illinois in 1919 and was graduated with a Bachelor of Science degree in Mechanical Engineering in 1923.

After spending five years in industry in engineering design, petroleum refining, lubricant sales, and boiler sales he returned to his alma mater in 1928, and has since been teaching power plant engineering, power laboratory, thermodynamics, and petroleum engineering in the Department of Mechanical Engineering. He has developed and has been in charge of the Petroleum Production Engineering courses at the University of Illinois since 1935.

He is a member of Tau Beta Pi, Pi Tau Sigma, Sigma Xi, American Society of Mechanical Engineers and American Society for the Promotion of Engineering Education.

Previous research has been in the line of boiler water conditioning. Published articles have included:

"Decomposition of Sodium Carbonate in Steam Boilers," A.S.M.E. "Transactions", V. 54, p. 171.

"Decomposition of Dilute Sodium Carbonate Solutions at Temperatures between 147° and 243° C," "Ind. and Engr. Chem.", V. 24, p. 1416. Co-author—F. G. Straub.

"Checking Up on the Orsat," "P. P. Engr.", V. 39, p. 409.

"Aluminum Paint on Oil Field Boilers," "Petroleum Engineer", Feb. 1938.

"Graphic Interpretation of Evaporation Losses from Vented Tanks," "Petroleum Engineer", Nov. 1939.

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